INVESTIGATIONS

ON

SORBIC AND PARASORBIC ACIDS.

INAUGURAL DISSERTATION

FOR THE ATTAINMENT

OF THE

DEGREE OF DOCTOR OF NATURAL SCIENCES

AT THE

UNIVERSITY OF TÜBINGEN,

UNDER THE PRESIDENCY

OF

DR. RUDOLPH FITTIG,

PROFESSOR IN ORDINARY OF CHEMISTRY,

PRESENTED

BY

J. B. BARRINGER,

OF SCHENECTADY, N. Y.

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The following investigations, which I have the honor of presenting to a highly distinguished faculty, as an Inaugural Dissertation for the degree of Doctor of Natural Sciences, were undertaken at the suggestion of Prof. Fittig; I would take this opportunity of expressing to him my cordial thanks for the uniform kindness and care which he has manifested towards me, during my course at the universities of Göttingen and Tübingen.

The manifold compounds which occur in plants form a class of bodies second to none in interest or importance. Repesentatives of almost all the known classes of organic compounds have been discovered; carbohydrides, acids, glucosides and alkaloids occur in great abundance; aldehydes, acid anhydrides and ethers have also been found; and an aceton has been obtained from the volatile oil of ruta graveolens. A great drawback to the study of these compounds is the extreme difficulty in many cases of obtaining sufficient material for a thorough investigation; and to this circumstance the comparative neglect of this branch of organic chemistry is in great part attributable. But that satisfactory results can be obtained is patent to every one conversant with chemical literature, and the few works which we possess on this subject have contributed largely to our chemical knowledge. Many have proved of great value to medecine and agriculture, and we may hope that all will hereafter be of service in helping to unriddle the mysterious processes of plant life.

Sorbic acid, the subject of the following investigation, was first obtained by HOFFMAN [1]) in the year 1859, from

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1) Ann. Ch. u. Pharm. 110. 129.

the socalled parasorbic acid, a name given by HOFFMAN to the volatile oil which occurs in the berries of the mountain ash.

„When the liquid which remains after partially satu-„rating the juice of the unripe berries with milk of lime „is left to stand until all the neutral calcium malate is „deposited from it, and then destilled in a copper vessel, „ultimately with the addition of a little sulphuric acid, „an acid destillate is obtained, from which after saturation „with sodium carbonate and evaporation, a brown oil is „separated by sulphuric acid; and by dissolving this oil „in ether, leaving the ether to evaporate and rectifying, „a transparent colourless oil is obtained consisting of „parasorbic acid $C^6 H^8 O^{2\alpha}$.[1]) Of this oil we shall speak hereafter. At present we are only interested to know that when it is boiled with solid potassium hydrate or strong chlorhydric acid it is converted into sorbic acid, a solid body, possessing the properties of a monobasic, monatomic acid, and easily obtainable in large white needles which fuse at 134^0. 5. It is difficultly soluble in cold water but dissolves easily in hot water, alcohol and ether. — From a boiling mixture of one volume alcohol and two volumes water it may be obtained in crystals an inch long. To these properties, as given by HOFFMAN, I have only to add that it is volatile with the vapours of water and that its boiling point is 228^0—230^0. It cannot however be destilled without suffering partial decomposition, a considerable portion always bieng converted into a yellow transparent resin, which remains behind in the bulb.

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1) Watts Dict. Chem. article Sorbic Acid.

Several derivatives were obtained by HOFFMAN, and the acid was investigated as accurately as the small amount of material at disposal and the state of chemistry at the time allowed. Since then it has become of great interest as being, empirically at least, the lowest homologue known of the interesting series of acids obtained by OVERBECK [1]), SCHROEDER [2]) and HAUSSKNECHT [3]) by the action of alcoholic potash on the dibromides of the corresponding members of the oleic acid group, and represented by the general formula $C^n H^{2n-4} O^2$. The present work was undertaken with the object of determining more accurately the analogies of sorbic acid — to determine whether it was really a member of the palmitolic acid group, or whether, as from its formula appeared not impossible, it might not be a representative of a new class of bodeis, which would occupy a position intermediate between the marsh gas and the benzol compounds [4]). The experiments performed have sufficiently shown that it is to be assigned a place in the palmitolic acid group. As will be seen its properties differ in some respects from those of the other members of the group but anomalies of this sort are frequently met with and are no doubt attributable to a difference in the structure of the molecules of the homologous bodies.

It afterward appeared advisable to make a few experiments with parasorbic acid in order to determine its true chemical character. These have proved in the most simple and convincing manner that this compound does not exist,

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1) Ann. Ch. Pharm. 140. 39.
2) Ann. Ch. Pharm. 143. 22.
3) Ann. Ch. Pharm. 143. 40.
4) Compare Hoffman Ann. Ch. Pharm. 110. 139.

it being nothing more than a mixture of sorbic acid with at least two other substances.

On the Action of Nascent Hydrogen on Hydrosorbic acid.

A small quantity of well crystallised sorbic acid was introduced into a flask with water and sodium amalgam. The amalgam was allowed to act for about eighteen hours— The solution was then acidified with sulphuric acid, and subjected to destillation with a large quantity of water. The destillate appeared somewhat turbid from an oil, which was held in suspension in the water; it reacted strongly acid and possessed a sweaty disagreeable smell. It was neutralised with sodium carbonate and evaporated to dryness; the residue was dissolved in a small quantity of water and the filtered solution acidified with sulphuric acid; an oil immediately separated, which was taken off with a pipette.

A larger quantity was now subjected to the action of sodium amalgam for several days; the product of the reaction was separated as above. After being taken off with a pipette it was washed once with about its own volume of water and dried over fused calcium chloride. It was then subjected to destillation in a Würtz destilling bulb. The temperature rose rapidly to 201° at which point it remained stationary. The fow drops which had already passed over were set aside and the receiver changed as soon as the temperature became constant. All the remaining liquid went over at 201°, the mercury remaining perfectly stationary. This latter portion was

allowed to stand in contact with fused calcium chloride for twenty four hours and then analysed.

Combustion.

I. . 1779 gm. gave on combustion with copper oxide . 1351 H^2 O and . 4164 C $O^{\cdot 2}$

II. . 2389 gm. gave . 1868 H^2 O and . 5545 C O^2

Found		Calculated for C^6 H^{10} O^2
I.	II.	
C 63.83	63.45	C 63.15
H 8.43	8.70	H 8.77

It appears then that an assimilation of two atoms of hydrogen has taken place. This result was rather unexpected as stearolic and behenolic acids do not combine with hydrogen. (The experiment does not seem to have been made with palmitolic acid).

The compound thus obtained is a colourless oily liquid, possessing a sweaty smell and a decided acid reaction. It is volatile with the vapours of water, and can readily be obtained in a pure state by virtue of this property. Its boiling point is 201^0 (cor. 204^0. 5); specific gravity = 0. 969 at 19^0. It does not solidify when exposed to a temperature of — 18^0, nor are any signs of crystallisation perceptible. It is easily soluble in alcohol and ether, but dissolves difficultly in water. It expels carbonic acid from the carbonates and forms well defined salts. It is monobasic.

Two acids of the formula C^6 H^{10} O^2 are already known viz: pyroterebic and ethylcrotonic acids.

Pyroterebic acid was first obtained by Rabourdin

and was afterwards investigated by CHAUTARD;[1]) our knowledge of this substance is however still very limited. It is produced by the dry destillation of terebic acid which is itself obtained by oxidising oil of turpentine with nitric acid

$$C^5 H^8 (C O H O)^2 = C^5 H^9 C O H O + C O^2$$

CHAUTARD describes it as a colourless oily liquid, heavier than water, smelling of butyric acid and boiling at 210°.

Ethylcrotonic acid was obtained by Frankland and DUPPA[2]) by the action of phosphor terchloride on leucic (diethoxalic) ether —

$$3 C^5 H^{10} (H O) C O (C^2 H^5) O + P Cl^3 = 3 C^5 H^9 C O (C^2 H^5) O + 3 H Cl + P H^3 O^3$$

The molecule of diethoxalic ether simply loses the elements of one molecule of water; the phosphor terchloride acting here as a dehydrating agent. — The acid itself is obtained from the ether thus formed in the usual manner, by boiling with a strong solution of potassium hydrate. „It crystallises very easily after fusion in large „brilliant four sided prisms which fuse at 39°.5 and „possess a peculiar smell, somewhat like that of a mixture „of pyrogallic and benzoic acids: It sublimes at ordinary „temperatures; it is easily soluble in alcohol and ether, „but only slightly in water". This compound is peculiarly interesting not only from its mode of formation, but also because from the products it forms when fused with potassium hydrate and the known constitution of dieth-

1) Jahresber. f. Ch. 1855. 652.
2) Ann. Ch. Pharm. 136. 1.

oxalic acid, we are enabled to determine its constitutional formula. I shall retum to this point again.

As will be seen further on our acid reacts differently from the pyroterebic and ethylcrotonic acids when it is fused with caustic potash. This taken in connection with the other differences in the properties of the three acids can leave no doubt that we have obtained a third representative of the acids $C^5 H^9 C O H O$. I have given to the new compound the name of hydrosorbic acid in accordance with the mode of its formation.

Salts of Hydrosorbic acid.[1])

Calcium Hydrosorbate. $Ca (C^6 H^9 O^2)^2 + H^2 O$.

Obtained by boiling a watery solution of the acid with powdered calc spar. It is easily soluble in water. I was unable to obtain it in good crystals. On evaporating its solution on the water bath it separates in concentric needles, which however can not be separated from the skin which forms upon the surface at the same time. If the solution is allowed to stand for several hours after only a small quantity of the salt has separated it redissolves. It appears to contain one molecule of water of crystallisation. It melts at about 125° to a pasty liquid.

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1) The liquid which remained after the hydrosorbic acid had been taken off with a pipette, together with the wash water, was destilled again with the vapours of water and the destillate used for preparing salts. The small quantity of fluid which had gone over, on destilling the dried acid, under 201° was also used for this purpose as it was thought to be only contaminated with a small quantity of water. Some of the pure acid was also used.

Analysis.

I. The salt was dried 48 hours over sulphuric acid and then heated to 120°—125° until the weight became constant —

. 27875 gm lost . 0163 = 5.84 p. c. H^2O

. 26245 gm anhydrous salt gave . 13325 $CaSO^4$ =

. 0391 Ca = 14.89 p. c.

II. The salt was dried 120 hours over sulphuric acid and then heated to 125° until the weight became constant —

. 2490 gm lost . 0139 = 5.58 p. c. H^2O

. 2351 gm anhydrous salt gave . 1197 Ca S O^4 =

. 0352 Ca = 14.97 p. c. —

	Found		Calculated
	I.	II.	
H^2O	5.84	5.58	6.33
Ca	14.89	14.97	15.03

Barium Hydrosorbate Ba $(C^6 H^9 O^2)^2$.

Obtained by neutralising a watery solution of the acid with barium carbonate. It is very soluble in water and can easily be obtained in small groups of needly crystals by allowing the saturated boiling solution to cool. It melts above 265° suffering decomposition at the same time. It is anhydrous.

Analysis.

The salt was dried 84 hours over sulphuric acid; it lost nothing in weight on being heated to 125° —

. 2387 gm gave . 1530 $BaSO^4$ = . 0899 Ba = 37.66 p. c.

Found	Calculated
37.66	37.74

Silver Hydrosorbate $Ag\ C^6\ H^9\ O^2$.

This salt is obtained as a white precipitate when silver nitrate is added to a solution of calcium hydrosorbate. It is more easily soluble in hot water than in cold, but it could not be obtained crystallised. It decomposes when heated for some time to 100°.

Analysis.

I. The salt was dried at 90°
.2182 grm. gave .1072 Ag = 49.12 p. c.

II. The salt was dried at 90°
.2348 grm. gave on combustion with copper oxide .0937 $H^2\ O$ and .2855 $C\ O^2$

	Found	Calculated
H	4.42	4.07
C	33.11	32.58
Ag	49.12	48.86

Copper Hydrosorbate. $Cu\ (C^6\ H^9\ O^2)^2$.

This salt was obtained as a green precipitate on adding copper chloride to a boiling hot solution of calcium hydrosorbate. It fused in the boiling liquid, and as appears from the analysis became thereby somewhat basic. In a dry state it is of a bluish green colour. On heating the dry salt its colour becomes a dark green, and the salt itself more and more basic the higher the temperature to which it is exposed.

At 185°—190° it fuses to a dark green fluid.

Analysis.

I. The salt was dried 48 hours over sulphuric acid
.2468 grm. gave .0697 $Cu\ O$ = .0556 Cu = 22.52 p. c.

II. The salt was dried one week over sulphuric acid .3105 grm. gave .0880 Cu O = .0702 Cu = 22.64 p. c.

Found		Calculated
Cu 22.52	22.64	21.90

.2468 grm lost after standing 48 hours over sulphuric acid, .0108 grm after being heated for 4 hours to 100°: on being exposed for 3 hours to a temperature of 130° a further decrease of .0351 grm was observed; a further exposure of 5¾ hours to a temperature of 140° brought the weight down .0269 more. On heating to 175° the salt decomposed. This loss in weight can evidently not be regarded as indicating the presence of water of crystallisation as the salt, when merely dried our sulphuric acid, already contained more copper than is required by the formula (see analysis).

On boiling the filtrate from the above salt a light green precipitate was formed which consisted of a much more basic salt than the one above analysed.

Analysis.

.1558 grm. dried over sulphuric acid gave .1051 Cu O = .0839 Cu = 53.20 p. c.

The neutral salt may have contained a small quantity of this latter as its precipitation took place in a boiling hot solution. This would account for the excess of copper found.

Sodium and potassium hydrosorbates were also made, but not analysed; they are both very soluble in water.

All the above salts of hydrosorbic acid feel greasy when rubbed between the fingers (like talc).

Hydrosorbic Ether $C^5 H^9 CO (C^2 H^5) O$.

A small quantity of pure hydrosorbic acid was dissolved in a flask in absolute alcohol and the solution saturated with dry chlorhydric acid gas, the necessary precautions being taken to prevent an elevation of temperature. The flask was then connected with an inverted Liebigs condenser and heated for about an hour on the water bath. The alcohol was then destilled off as much as possible, and the remaining liquid diluted with water containing a little sodium carbonate (in order to remove any free hydrosorbic acid which might be present). It was then shaken up with ether. After destilling off the ether the fluid which remained was dried by means of fused calcium chloride and subjected to destillation. The thermometer rose gradually to 166° at which point it become stationary; the receiver was then changed; the liquid remaining in the bulb all destilled over between 166° and 167°. This latter portion was again dried over fused calcium chloride and analysed.

Combustion.

.2299 grm. gave .2025 $H^2 O$ and .5681 $C O^2$

	Found	Calculated
H	9.78	9.85
C	67.37	67.60

Hydrosorbic ether is a colourless liquid, possessing a pleasant fruity smell, and boiling at 166°—167°. Its specific gracity is less than that of water. It is easily soluble in alcohol and ether, but only difficultly soluble

in water. It appears to form a compound with calcium chloride; a small quantity of the ether, which had stood for some time in contact with this salt, become filled with crystals which dissolved slowly in water, a considerable quantity of the ether separating at the same time. Acetic ether also possesses this property of forming a crystalline compound with calcium chloride.

It was found to be impossible to obtain a compound containing more hydrogen, by the action of sodium amalgam on sorbic acid. In one case the amalgam was allowed to act for ten days, but hydrosorbic acid was again obtained. Hydrosorbic acid behaves in this respect precisely as its homologues, oleic acid etc., none of which combine with hydrogen (except acrylic and perhaps crotonic acid) [1]). To trace the analogy still further it was resolved to investigate the action of bromine on hydrosorbic acid, and of alcoholic potash on the dibromide, which it was hoped would be formed. As was expected the acid combined readily with two atoms of bromine and the dibromide thus obtained was easily converted into sorbic acid when boiled with alcoholic potash. Before describing these experiments it will to well perhaps to make a few remarks on

A Byproduct in the preparation of Hydrosorbic acid.

Hydrosorbic acid is not the only compound formed by the action of sodium amalgam on sorbic acid. The

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1) Acrylic Ann. Ch. Pharm. 125. 307; crotonic ibid 137. 233 and 139. 62 angelic ibid. 135. 291: oleic ibid 140. 39; Erucic ibid. 135. 226.

watery fluid, which remains in the flask after the hydrosorbic acid has been destilled off, yields when shaken up with ether a small quantity of an oil which is heavier than water. It is inodorous, possesses a strong acid reaction, and is insoluble in cold water but dissolves easily in alcohol and ether. It cannot be destilled without suffering decomposition. A brownish oil goes over which is lighter than water, and a coaly residue remains behind in the destilling bulb.

The barium salt was made by boiling the acid with water and barium carbonate; it is easily soluble in water and could not be obtained in good crystals. It separates on evaporating its solution in warty crusts. A barium estimation showed that it contained exactly as much barium as barium hydrosorbate.

Barium estimation

.2518 grm. dried over sulphuric acid lost nothing at 100°.

.2518 grm. gave .1605 B a S O^4 = .0943 B a = 37.45 p. c.

The calcium salt was made by boiling the acid with water and powdered calc spar. It could not be obtained crystallised and was therefore not analysed.

The further investigation of this compound was given up, as I noticed that some of it, which had been sealed up in a tube with water and allowed to lie several weeks, had partially solidified under the water. The quantity obtained was too small to allow of the separation of the compounds occuring therein in case it was a mixture.

It may have been a polymer of hydrosorbic acid. It could hardly have been isomeric with capronic acid, (the

barium determination would agree as well with the formula $(C^6 H^{11} O^2)^2 Ba$ as with $(C^6 H^9 O^2)^2 Ba$ as this would no doubt have been volatile with the vapours of water.

On the action of Bromine on Hydrosorbic acid.

A small quantity of pure hydrosorbic acid was cooled off with ice water, and a quantity of bromine equivalent to one molecule of the acid added in small quantities (1.5 grm. of bromine was taken to every gramm of the acid). The reaction was quite violent and the formation of a small quantity of bromhydric acid could not be prevented. (In another experiment the acid was cooled off with a mixture of ice and common salt; but small quantiteis of bromhydric acid were formed even then). The product of the reaction was a viscous liquid, heavier than water and insoluble therein. When freed from all excess of bromine it was perfectly colourless. It showed no signs of crystallisation when exposed to a temperature of -17^0 and remained liquid after standing for several days in vacuo over sulphuric acid and caustic lime. It appeared to be volatile with the vapours of water. Its investigation was thought to be unnecessary as it was without doubt hydrosorbic acid dibromide ($C^6 H^{10} Br^2 O^2$) containing perhaps a small quantity of bromine substitution compounds.

On the action of Alcoholic Potash on Hydrosorbic acid dibromide.

The dibromide, obtained as above, was introduced into a flask with alcohol and a quantity of potassium

hydrate sufficient to form monobromhydrosorbic acid (two molecules potassium hydrate and one molecule dibromide). The solution was then boiled for several hours on the water bath, the flask having been previously connected with an inverted condenser in order to prevent the volatilisation of the alcohol. The alcohol was then destilled off. On acidifying the residue with chlorhydric acid a heavy oil separated. In order to separate any sorbic acid which might have been formed, the whole product was destilled with the vapours of water. Everything went over however. The destillate was therefore shaken up with ether, and the oil which remained after the ether had been destilled off allowed to stand for a week over sulphuric acid. At the end of this time crystals had made their appearance. The oil was poured off and the crystals well pressed between filtering paper; they were then recrystallised from water. They were difficultly soluble in cold water, but dissolved easily on boiling, separating again as the solution cooled in beautiful white needles which fused at 132° — 134° and contained no bromine. This substance was without doubt sorbic acid. A combustion was not considered necessary.

The oily acid spoken of above was probably monobromhydrosorbic acid. The quantity obtained was too small to permit of its investigation. An attempt was made to prepare the calcium salt but it could not be obtained in a state fit for analysis.

As the potash seemed to act too energetically, a portion of the dibromide being converted into sorbic acid, although the quantity of potash taken was rather less than more than the theoretical quantity, it was resolved

to try the action of water on the dibromide. A portion was therefore sealed up in a tube with water and heated to about 150° for six or eight hours. The tube was then opened, the contents neutralised with sodium carbonate, the solution evaporated to a small volume and acidified with sulphuric acid. Nothing separated although a large quantity of an oil was present in the tube before neutralisation. Ether extracted nothing from the fluid.

Much surprised at this result I heated another portion with water in the same manner. After several hours the tube was opened. An oil still remained under the water. The supernatant fluid was poured off, the oil washed with a small quantity of water and then dissolved in a cold solution of sodium carbonate, the slightly alkaline liquid was heated for about ten minutes in a flask which was connected with a condenser. A small quantity of an oil had destilled over. The fluid in the flask was found to have acquired a strong acid reaction. It was again neutralised and destilled with the vapours of water until the destillate was perfectly clear. (Care was taken that the fluid in the flask always retained an alkaline reaction). The destillate gave on being shaken up with ether a small quantity of a sweet smelling neutral oil. The residue in the flask was acidified and shaken up with ether. I obtained after destilling off the ether a resinous residue possessing a strong acid reaction.

The fluid which had been decanted from the oil which remained in the tube after heating the dibromide with water yielded nothing when shaken up with ether.

The dibromide was now heated to 150° in a sealed tube with sodium carbonate; I obtained however no definite

product. The neutral oil was again formed in small quantities.

I am unable to say what reaction takes place here. It may be that the water at 150° exercises no action on the dibromide, but that on being boiled with a solution of sodium carbonate it loses carbonic anhydride, monobromamylen being formed. This supposition would of course imply that a molecule of bromhydric acid should also be given off. It would explain the fact that so little of the above mentioned neutral oil was obtained, as the boiling point of a compound of the formula $C^5 H^9 Br$ would be low and the greater part could escape during destillation. JAFFE [1]) has moreover observed that on boiling the potassium salt of angelic acid dibromide a volatile oil, boiling between 80° and 90°, is formed, which he considers to be a monobrombutylen, carbonic anhydride being at the same time evolved. I could not obtain enough of the oil to determine whether it was really monobromamylen.

The experiments just described prove that hydrosorbic acid is a true homologue of oleic, erucic and hypogaic acid. Its easy assimilation of two atoms of bromine, and the facility with which the dibromide thus formed loses two molecules of bromhydric acid under the influence of alcoholic potash, thus regenerating the corresponding acid of the group $C^n H^{2n-4} O^2$ (viz: sorbic acid), together with its incapability of combining with

1) Ann. Ch. Pharm. 135. 291. Compare Jaffe's statement that SCHMIDT and ERLENMEYER had obtained an oil $C^8 H^7 Br$ by a similar decomposition from bromcinnamic acid.

hydrogen, render its analogies with these acids too apparent to be overlooked.

On the action of fused Potassium hydrate on Hydrosorbic acid.

The great aim of modern chemistry is the determination of the constitutional formulae of bodies. Not content, as was formerly the case, with merely discovering a substance, or even of determining its empirical formula and its reactions with the ordinary reagents, we now demand to know how the atoms are held together in the compound, we seek to determine its analogies with other substances already known. Until this was recognised as the fundamental principle of all chemical research, chemistry can not be said to have been a science, and not until we posess data of this kind applying to the larger proportion of compounds, shall we have a true chemical theory, a theory from which all known facts may be deduced. The results already obtained are enormous, when we consider the short time that has elapsed since chemists first recognised this principle, but a vast deal of labor still remains to be done.

A reaction which has long been looked upon with great favour, and which has been used particularly to determine the constitutional formulae of the acids $C^n H^{2n-2} O^2$ is the action of fused potassium hydrate on compounds. The reaction may be looked upon as an addition of $H^2 O^2$ to the molecule of the compound.

$C^4 H^6 O^2$ (Methacrylic acid) $+ 2KHO = KCO^2H + KC^3H^5O^2 + H^2$

$C^6 H^{10} O^2$ (Ethylcrotonic acid) $+ 2KHO = C^2H^3KO^2 + C^4H^7KO^2 + H^2$.

It was determined to investigate its action on hydrosorbic acid.

A quantity of the acid was therefore dissolved in a large excess of potash and the solution evaporated to dryness. The residue was then heated for 10 or 12 hours in a silver crucible to a temperature of 170°. It was found however that no decomposition had taken place, as on destilling the mass with water, after acidifying with sulphuric acid, hydrosorbic acid was found in the destillate. The mixture was then fused over the gas lamp (care being taken to keep the temperature as low as possible) until the evolution of gas ceased. The mass was then dissolved in water, and the solution acidified and destilled until the destillate no longer reacted acid. The destillate was divided into three equal portions; one portion was neutralised with sodium carbonate, the other two added, and the whole again destilled to a small volume. The fluid remaining in the flask necessarily contained the sodium salt of the strongest acid, in case two acids had been formed. It was evaporated to dryness, and the residue carefully dried over the gas lamp. It was then dissolved in water and silver nitrate added to the filtered solution. The precipitate which formed was filtered off, well pressed, and dissolved in boiling water. The salt separated, as the filtered solution cooled, in small dull feathery crystals which blackened when exposed to the light. A silver estimation showed it to be silver butyrate.

Silver estimation.

I. .1898 grm. dried at 100° gave .1062 Ag = 55.95 p. c.

II. .1765 grm. dried at 100° gave .0977 Ag = 55.36 p. c.

	Found		Calculated
Ag	55.95	55.36	55.38

The destillate from this salt was divided into two equal portions; one was neutralised with sodium carbonate, the other added and the whole destilled to a small volume. The destillate contained the weaker acid. It was neutralised with sodium carbonate and the silver salt prepared as above. This salt also took the form of dull feathery crystals which blackened on exposure to light, and proved to be also silver butyrate.

Silver determination

.2851 grm. dried at 100° gave .1584 grm. Ag = 55.57 p. c.

Found	Calculated
55.57	55.38

One can hardly assume that both or one of the salts analysed was impure, and that it was a mere accident that they possessed the composition of silver butyrate. But in order to solve all doubts the silver salt of the third portion was prepared. It possessed exactly the same properties as the two salts already analysed and proved to be likewise silver butyrate.

Silver determination.

.1798 grm. dried at 100° gave .9940 Ag = 55.28 p. c.

Found	Calculated
55.28	55.38

This result was entirely unexpected and at first sight inexplicable, as it could not be seen how butyric

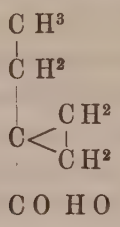
acid alone could be obtained from a compound containing six atoms of carbon. It was at first thought that acetic acid had also been formed but had been decomposed by reason of a too high temperature. This however is exceedingly improbable, as the temperature was kept as low as possible, and it is a well known fact that sodium acetate, when heated with a mixture of caustic potash and lime, does not decompose until a very high temperature has been obtained.

On more careful consideration it was found that if we adopt two hypotheses, which seem to be generally held by chemists viz. that no compound of carbon, with so called free affinities can exist (a more intimate union of the carbon atoms always taking place in such cases), and again that in the decomposition of the acids $C^n H^{2n-2} O^2$ by means of fused potassium hydrate, the molecule always breaks up at that spot where the double union of the carbon atoms occurs.[1]) I say, if we adopt these very

1) Marasse, Berl. Ber. 1869. 359; Ad. Claus ibid 1870. 180; Paterno ibid. 1870. 93; KEKULÉ ibid. 1870. 604. — That the first of the above hypotheses is true is rendered extremely probable by the difficulty which we frequently experience in saturating these so called free affinities. The acids $C^n H^{2n-2} O^2$ for instance do not combine with hydrogen. No reason can be given why they should not do so in case they really contain gaps as was formerly held. Numerous instances of this sort are known, and we must therefore conclude that some force has to be overcorne before non — saturated compounds can unite with any thing, in other words that a more intimate union of the carbon atoms occurs in these compounds. — All facts at present known, with regard to the action of fused potassium hydrate on the acids $C^n H^{2n-2} O^2$ harmonise with the second of the above hypotheses with one exception. KEKULÉ states (loc. cit.) that he obtained only acetic acid from the crotonic acid which is formed by the condensation of aldehyd, and he therefore assumes in accor-

probable hypotheses, the reaction in question becomes not only perfectly clear, but we can also, with the help of this reaction, give the constitutional formula of hydrosorbic acid with almost absolute certainty.

Twenty five acids of the formula $C^6 H^{10} O^2$ are possible but only one of them can give under the suppositions made above solely butyric acid when fused with potassium hydrate viz: the acid with the formula



A compound with this formula would necessary split up so as to give normal butync acid and two molecules of formic acid, which latter would be immediately converted into $C O^2$ and water. I am unable to say whether the

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dance with the above hypothesis, that the formula of his acid is $C H^3 — C H = C H — C O H O$. If this be so we must assume that in the formation of crotonic acid from cyanallyl, (no doubt seems to exist as to the identity of the two acids) a molecular rearrangement takes place. Assuming this to be the case here however we should be equally justified in assuming it in other and all cases, and all conclusions which have been made as to the formulae of bodies obtained from the cyanogen compounds of alcohol radicles would be worthless. It appears much more probable that a molecular rearrangement should take place in the reaction with fused potash than in that with the cyanogen compound. Claus however (loc. cit.) states that he obtained propionic and carbonic acids from the crotonic acid prepared from cyanallyl. This would agree with the formula $C H^2 = C H — C H^2 — C O H O$. A repetition of these experiments is very desirable and of great importance for theoretical chemistry.

butyric acid obtained was really the normal. A decision of this question appears very desirable and will be undertaken at the earliest opportunity.

As regards the constitutional formulae of pyroterebic and ethylcrotonic acids we have positive evidence only concerning the latter. It was obtained by Frankland and Duppa by treating diethoxalic ether with phosphor terchloride; the reaction is as follows:

$$C\begin{cases}C^2H^5\\C^2H^5\\CO\,HO\end{cases} HO = C\begin{cases}=C^2H^4\\-C^2H^5\\CO\,HO\end{cases} + H^2O$$

It gives on fusion with potash acetic and butyric acids. Its formula must therefore be —

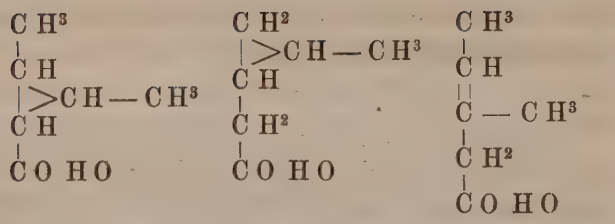
$$C\begin{cases}=CH-CH^3\\-CH^2-CH^3\\CO\,HO\end{cases}$$

This is the same formula as that adopted by F. & D. translated into our present method of writing formulae —

Pyroterebic acid can have any of the seven following formulae (these being the only ones which would give acetic and butyric acids) —

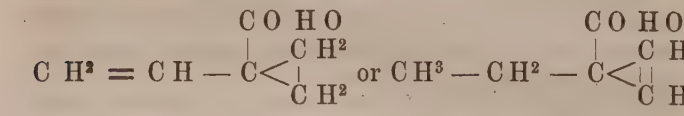
1	2	3	4
CH^3	CH^3	CH^3	CH^3
CH^2	CH^2	$CH-CH^3$	CH
$C=CH-CH^3$	CH^2	CH	CH
$CO\,HO$	CH	CH	$CH-CH^3$
	CH	$CO\,HO$	$CO\,OH$
	$CO\,HO$		

5 6 7



Numbers 1, 2, 5, 6, 7 would give normal butyric acid, numbers 3 and 4 isobutyric acid. Which was obtained from pyroterebic acid is unknown.

It seems almost useless to speculate on the formula of sorbic acid. Marasse found that stearolic acid gave on fusion with potash myristinic acid, and concludes therefore that it (stearolic) contains the group C = C twice and not the group C ≡ C; for in this case he should have obtained palmitic acid. — If these experiments are regarded as conclusive sorbic acid would have most probably the formula



Speculations of this sort are however of little value at present.

On the action of Bromine on Sorbic acid.

Palmitolic, stearolic and behenolic acids are characterised by the facility with which they combine with two and four atoms of bromine. I have made numerous attempts to obtain the corresponding compounds of sorbic

acid, but have only succeeded in obtaining a small quantity of the tetrabromide.

The first experiments were made by allowing one molecule of bromine to act upon one molecule of sorbic acid in ethereal solution. (Ether was used as the acid was so difficultly soluble in cold water.) On destilling off the ether an oil remained behind, which became solid when exposed to a temperature of 0^0. On exposing the mass afterwards to the ordinary temperature of a room it became pasty, but did not again liquefy. It gave off bromhydric acid on being allowed to stand in vacuo over sulphuric acid, inasmuch as the paper with which the vessel was covered was entirely eaten up after 36—48 hours. On being brought into contact with water it gave off dense fumes.

A portion of the product thus obtained was dissolved in a cold solution of sodium carbonate; a small quantity of an oil, which remained undissolved, was filtered off and the clear filtrate acidified with sulphuric acid. An oil was thrown down, which became solid after about thirty six hours. It was filtered off, well pressed between filtering paper, and dissolved in boiling water, care being taken to prevent the loss of any volatile compound by attaching the flask containing the solution to a condenser. On boiling the acid with the water it at first liquefied, and then gradually dissolved up; a small black insoluble residue was filtered off and the filtrate allowed to cool. White needly crystals separated, which after one recrystallisation were found to fuse at 131^0; they contained no bromine and were no doubt sorbic acid which had not been acted upon.

The filtrate from these crystals was destilled down to a small volume, and then again filtered and allowed to cool. More sorbic acid was obtained. The filtrate was then evaporated to dryness on the water bath. It turned brown as it became concentrated and finally decomposed giving off dense fumes, which did not appear to arise altogether from bromhydric acid; a coaly residue remained.

In one experiment instead of evaporating to dryness, I shook up the last residual fluid with ether and obtained a brownish resin. On drying this on the water bath a crystalline substance was volatilised and deposited on the edge of the evaporating dish. Of this I only obtained enough to determine its fusing point, which was found to be about 110°. Whether this was not also impure sorbic acid is perhaps a question; the quantity obtained was too small to permit me to purify it by recrystallisation.

The destillate which was obtained in the above process reacted acid, and gave with silver nitrate, a precipitate insoluble in nitric acid. A portion of the destillate was shaken up with ether, until all matter which coloured the ether had been removed, and a fresh quantity of ether and some chlorine water then added. The ether was coloured yellow. Bromhydric acid was therefore present, having been formed by the action of the boiling water on the compound or compounds at first produced.

The whole destillate was then made alkaline with sodium carbonate and shaken up well with ether. On destilling off the ether an oil remained behind, which possessed the smell of a fruity ether. It was dried by means of fused calcium chloride and then destilled; a considerable quantity went over at about 40°; (ether or

bromethyl?); the temperature then rose rapidly to 180°. Here the destillation was stopped as the residue began to decompose. A tarry destillate was obtained. This compound was possilby the ether of some acid; as the ether used as a solvent for the sorbic acid contained some alcohol, and, as we have seen, bromhydric acid appears to have been formed by the action of the bromine on the sorbic acid, the conditions of the experiment were favourable to the formation of an ether.

The fluid, after having been shaken up with ether as above, was then acidified and again shaken with ether; the residue obtained on destilling off the ether was solid; it was dissolved in hot water and the solution allowed to cool. Needles separated, which fused at 127° — 130°; they contained no bromine and were without doubt merely sorbic acid. The filtrate was neutralised with sodium carbonate, evaporated to a small volume and acidified with sulphuric acid. I obtained a brownish substance, but in so small a quantity that its investigation was impracticable. Several experiments like the above were made but I always obtained a large quantity of resinous matter and considerable sorbic acid remained unacted upon. No well defined compound containing bromine could be obtained.

I now made an attempt to obtain the tetrabromide; the experiment was made in the same manner as above with an ethereal solution of sorbic acid; the quantity of bromine taken was of course equal to two molecules to one of the acid. On destilling off the ether large quantities of bromhydric acid were evolved. It was completely driven off on the water bath. The residue became solid

on cooling. It was coloured yellow, but became perfectly white when moistened with a little water. It smelt like camphor. It was not complelety soluble in sodium carbonate. On destilling it with the vapours of water an oil went over; this may have been an ether again. Here again I obtained mainly resin; but a small quantity of a substance, fusing at about 186° was also obtained.

I then determined to attempt to make the tetrabromide without using ether. For this purpose five grammes of sorbic acid were rubbed together in a mortar with 15 gm. (two molecules) of bromine until the colour of the bromine had entirely disappeared. Considerable heat was generated by the operation. The product was a white solid, which remained undissolved in the water. The water was poured off; it contained a large quantity of bromhydric acid. Ether extracted only a little oil from it.

The solid product obtained was very difficultly soluble in water but dissolved easily in alcohol and benzine (boiling from 116° — 135°). It was found however that it could not be obtained in crystals from its alcoholic solution. The alcohol seemed also to decompose it somewhat as it no longer dissolved complelety in sodium carbonate after the alcohol had been driven off.

In order to free it from any neutral body which might be present it was dissolved in a cold solution of sodium carbonate, and the alkaline fluid shaken up with ether. A very small quantity of a yellowish oil was obtained. The salt was then decomposed with sulphuric acid. An oil was precipitated which was extracted by means of ether. The residue remaining after destilling off the ether partially solidified, on being allowed to stand

over sulphuric acid. It could not be destilled without decomposition.

The whole mass was now dissolved in dilute alcohol. It invariably separated as a heavy oil, no matter whether the hot clear solution was allowed to cool, or the clear cold solution to evaporate over sulphuric acid. The upper liquid was poured off; the oil soon became almost solid; it was carefully pressed and again dissolved in alcohol and water; after repeating this process twice I obtained with the oil a small quantity of a hard solid substance. This was carefully separated from the oil and dissolved in pretty strong alcohol. I obtained first a small quantity of oil; then beautiful large transparent crystals which fused at 181° — 186°. The best crystals were picked out and the others recrystallised. They now fused at 178° — 179° but became somewhat viscous at about 140°. They probably still enclosed traces of the oil. It was impossible to suspect that the two substances were not identical in spite of the difference in their melting points. The pure substance would probably fuse at about 184°. By operating in this manner, namely allowing the alcoholic solution to evaporate spontaneously, pouring off the upper liquid (which was evaporated still further), pressing the partially solidified oil between filter paper and then recrystallising it from rather dilute alcohol until the hard monoclinic crystals made their appearance, I obtained enough of the substance for a couple of combustions and a bromine estimation. Only well formed crystals were taken every one being carefully examined.

Combustion and bromine estimation.

It lost nothing at 100° —

I. .24275 gave .04265 H^2 O and .15285 C O^2

II. .2137 gave .03575 H^2 O and .1312 C O^2

.2729 gave .4728 Ag Br = .2012 Br

	Found		Calculated for C^6 H^8 Br^4 O^2
C	17.17	16.74	16.66
H	1.95	1.86	1.85
Br	73.73		74.07

The substance was therefore sorbic acid tetrabromide. It crystallises in beautiful large transparent crystals, which appear to be a combination of a monoclinic prism ∞ P with the pinakoid 0P; its fusing point is probably about 184°. It is easily soluble in alcohol, and after having been freed from all oil dissolves easily in hot water, crystallising again as the solution cools in needles, which resemble those of sorbic acid. I unfortunately omitted to determine the melting point of these crystals; they were no doubt somewhat purer than those obtained from dilute alcohol, as the latter could easily enclose a trace of oil, which would exercise a great influence on the melting point.

It would be a very interesting experiment to investigate the action of alcoholic potash on this compound; we may expect it to lose four molecules of bromhydric acid, and to be converted into an acid C^6 H^4 O^2:

$$C^6 H^8 Br^4 O^2 - 4 Br H = C^6 H^4 O^2$$

This acid would be homologous with benzoic acid, it containing C H^2 less than that acid —

On the action of Nitric acid on Sorbic acid.

By treating palmitolic, stearolic and behenolic acids with nitric acid, Overbeck. Schröder and Haussknecht obtained three bodies from each acid; viz: an acid containing the same number of carbon and hydrogen atoms and two atoms of oxygen more than the original acid, a diatomic, dibasic acid containing half as much carbon as the original acid, and a substance, which they regarded as the aldehyde of this latter acid. The general reaction would be

$$2\,C^n\,H^{2n-4}\,O^2 + O^7 = C^n\,H^{2n-4}\,O^4 + C^{\frac{n}{2}}\,H^{\frac{2n-4}{2}}\,O^4 + C^{\frac{n}{2}}\,H^{\frac{2n-4}{2}}\,O^3.$$

A similar reaction, it was expected would take place with sorbic acid. Various experiments were made but they gave no positive result. Cold fuming nitric acid is without action on sorbic acid. The latter simply dissolves, being reprecipitated on the addition of water. On boiling the solution for a few moments until gas begins to be evolved, and then removing the flame, a stormy reaction sets in; red fumes are evolved and the sorbic acid seems to be completely destroyed. Lead acetate gave in the solution, after the reaction was completed, an abundant precipitate. On decomposing the precipitate however with sulphydric acid nothing but some resinous matter was obtained. In one experiment the lead salt was decomposed with sulphuric acid and the solution shaken up with ether. Nothing was obtained however. Several experiments were made with acids of various degrees of strength, but with no better success. If a dilute acid was taken, the sorbic acid could be boiled with it for

some time without any reaction taking place. Suddenly however red fumes would be evolved and the reaction could then not well be controlled. Before red fumes were evolved a volatile oil was observed in large quantities on the surface of the heated fluid. What this was is difficult to say. There would probably be little difficulty in isolating this compound.

Both time and material were lacking to pursue this reaction farther. These experiments cannot be regarded as of much value. The reaction is a so destructive one that large quantities of material must be taken in order to obtain any results.

On Parasorbic Acid.

It was thought to be desirable to make a few experiments which would establish the true nature of parasorbic acid. This is prepared according to Hoffman [1]) in the following manner. The acid destillate obtained as a by-product in the manufacture of malic acid (Sec. p. 2) is saturated with sodium carbonate and evaporated on the water bath. On treating the residue with moderately dilute sulphuric acid a brownish oil separates. This is purified by dissolving in ether, allowing the ether to evaporate spontaneously, and rectifying the residue. On destilling the acid so obtained a resinous transparent residue is always left behind, no matter how often or under what precautions it is destilled. H. states that when it has been freshly destilled it is a colourless liquid, with a peculiar aromatic smell, which in a dilute state is not unpleasant; in a concentrated state however the

1) Ann. Ch. Pharm. 110. 129.

vapours have a very disagreeable smell. Its boiling point is 221° and specific weight 1.068 at 15°. It is not very insoluble in water, but dissolves in every proportion in alcohol and ether; the solutions react acid. It dissolves in the caustic alkalies and alkaline earths; also in alkaline carbonate but does not expel the carbonic acid from the latter. All these solutions give resinous residues on evaporation. The free acid and the silver salt were analysed by Hoffman, and numbers closely approximating to those demanded by the formula $C^6 H^8 O^2$ obtained.

Its strange conversion into sorbic acid, together with the fact that it always left a resinous residue, no matter how often it was destilled, and that a similar residue was obtained when sorbic acid was destilled, awakened a suspicion that it might after all be nothing but impure sorbic acid.

I therefore undertook to prepare the barium salt. The acid was boiled in a flask with water and barium carbonate, the flask being connected with an inverted cooler, to prevent anything volatilising. A copious evolution of carbonic anhydride set in as soon as the fluid became warm. (Hoffman's statement that it dissolves in the alkaline carbonates without evolution of $C O^2$ is incorrect; as soon as the solution is warmed a copious evolution of gas sets in; indeed, as we have just seen, it even decomposes an insoluble carbonate). As soon as the liquid reacted neutral it was destilled with the vapours of water. An oil, most probably some hydrocarbon, went over which possessed the characteristic smell of parasorbic acid. Considerable resin remained undissolved. This was filtered off and the filtrate acidified with chlorhydric

acid. It acquired thereby a pungent smell (the same as that of parasorbic acid) and an oil was precipitated, which however became solid after a few hours. The fluid was shaken up with ether, and the mass which remained after destilling off the ether well pressed between filtering paper, in order to free it from a small quantity of a pungent oil. It was then dissolved in hot water; as the solution cooled it separated in beautiful long needles, which fused at 131°. A tube containing commercial sorbic acid was attached to the other side of the thermometer and the two substances heated in the same bath. They both fused at the same instant (131°) [1]).

We have thus in the simplest manner possible obtained sorbic acid directly from parasorbic acid; no one can say that a molecular rearrangement has taken place here.

Sodium amalgam was then allowed to act upon parasorbic acid. I obtained a product which resembled hydrosorbic acid in all respects. It was however evidently somewhat impure, and the barium salt was therefore made. This was obtained after several recrystallisations in needles, which were grouped together in the manner so characteristic for barium hydrosorbate. A barium determination proved it to be this salt.

Ba determination:

.2384 grm. dried over sulphuric acid lost nothing at 100°

.2384 gave .1520 Ba SO^4 = .0893 Ba = 37.46 p. c.

Found	Calculated
37.46	37.74

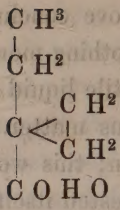
1) The commercial acid also possessed a slight pungent smell; after one recrystallisation from hot water it fused as H. states at 134°. 5.

These experiments prove conclusively that the so-called parasorbic acid is nothing more than a mixture of sorbic acid, with some volatile liquid compound (perhaps a hydrocarbon) and resinous matter. It is possible that another acid occurs therein; this would account for the pungent odour which manifested itself, when the barium salt of the crude acid was acidified. HOFFMAN states that he was unable to obtain any well defined salts; the reason of this was that he used the hydrated alkalies and alkaline earths; these would necessarily dissolve some, if not the greater quantity of the resin, which would prevent the salts from crystallising.

The facility with which sorbic acid is obtained when parasorbic acid is boiled with solid potassium hydrate is now easily explained. The potash would destroy the resinous matter, and the volatile oil would be driven off during the boiling, so that nothing would remain to hold the sorbic acid in solution when the product of the reaction was acidified, and it would necessarily separate in the solid form.

The results of the foregoing investigation may be summed up as follows.

1st. Sorbic acid readily combines with two atoms of hydrogen, being converted into an acid $C^6 H^{10} O^2$; this acid combines with two atoms of bromine, and the dibromide thus formed loses two molecules of bromhydric acid when boiled with alcoholic potash, being reconverted into sorbic acid. Hydrosorbic acid gives when fused with potassium hydrate only butyric acid; its constitutional formula is therefore



It is incapable of combining with hydrogen.

2nd. Sorbic acid combines with four atoms of bromine and forms a well characterised tetrabromide.

3rd. Parasorbic acid does not exist.

We are then amply justified in regarding sorbic acid as a member of the palmitolic acid group. Its capability of combining with four atoms of bromine, and its production from the corresponding member of the oleic acid group by the action of alcoholic potash on the dibromide, sufficiently prove this. It differs from its homologues in that it combines with two atoms of hydrogen; if palmitolic and stearolic acids are really incapable of assimilating hydrogen, this would indicate that some difference in molecular structure existed between them and sorbic acid.

The properties of hydrosorbic acid correspond closely with those of its homologues.

Nov. 22. 1870.